

NANO-POROUS METAL OXIDE SEMICONDUCTOR SPECTRALLY SENSITIZED WITH  
METAL CHALCOGENIDE NANO-PARTICLES

Cross-reference to related patent applications

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This application claims the benefit of U.S. Provisional Application No. 60/405,975 filed August 26, 2002, which is incorporated by reference. In addition, this application claims the benefit of European Application No. 02102129.0 filed August 13, 2002, which is  
10 also incorporated by reference.

Field of the invention

The present invention relates to a nano-porous metal oxide  
15 semiconductor in-situ spectrally sensitized with a metal chalcogenide.

Background of the invention.

20 There are two basic types of photoelectrochemical photovoltaic cells. The first type is the regenerative cell which converts light to electrical power leaving no net chemical change behind. Photons of energy exceeding that of the band gap generate electron-hole pairs, which are separated by the electrical field present in the  
25 space-charge layer. The negative charge carriers move through the bulk of the semiconductor to the current collector and the external circuit. The positive holes ( $h^+$ ) are driven to the surface where they are scavenged by the reduced form of the redox relay molecular (R), oxidizing it:  $h^+ + R \rightarrow O$ , the oxidized form. O is reduced back  
30 to R by the electrons that re-enter the cell from the external circuit. In the second type, photosynthetic cells, operate on a similar principle except that there are two redox systems: one reacting with the holes at the surface of the semiconductor electrode and the second reacting with the electrons entering the  
35 counter-electrode. In such cells water is typically oxidized to oxygen at the semiconductor photoanode and reduced to hydrogen at the cathode. Titanium dioxide has been the favoured semiconductor for these studies. Unfortunately because of its large band-gap (3 to 3.2 eV),  $TiO_2$  absorbs only part of the solar emission and so has  
40 low conversion efficiencies. Graetzel reported in 2001 in Nature, volume 414, page 338, that numerous attempts to shift the spectral response of  $TiO_2$  into the visible had so far failed.

Mesoscopic or nano-porous semiconductor materials, minutely structured materials with an enormous internal surface area, have been developed for the first type of cell to improve the light capturing efficiency by increasing the area upon which the spectrally sensitizing species could adsorb. Arrays of nano-crystals of oxides such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$  and  $\text{Nb}_2\text{O}_5$  or chalcogenides such as  $\text{CdSe}$  are the preferred semiconductor materials and are interconnected to allow electrical conduction to take place. A wet type solar cell having a porous film of dye-sensitized titanium dioxide semiconductor particles as a work electrode was expected to surpass an amorphous silicon solar cell in conversion efficiency and cost. These fundamental techniques were disclosed in 1991 by Graetzel et al. in *Nature*, volume 353, pages 737-740 and in US 4,927,721, US 5,350,644 and JP-A 05-504023. Graetzel et al. reported solid-state dye-sensitized mesoporous  $\text{TiO}_2$  solar cells with up to 33% photon to electron conversion efficiencies.

In 1995 Tennakone et al. in *Semiconductor Sci. Technol.*, volume 10, page 1689 and O'Regan et al. in *Chem. Mater.*, volume 7, page 1349 reported an all-solid-state solar cell consisting of a highly structured heterojunction between a p- and n-type semiconductor with a absorber in between in which the p-semiconductor is  $\text{CuSCN}$  or  $\text{CuI}$ , the n-semiconductor is nano-porous titanium dioxide and the absorber is an organic dye.

Furthermore, in 1998 K. Tennakone et al. reported in *Journal Physics A: Applied Physics*, volume 31, pages 2326-2330, a nanoporous n- $\text{TiO}_2$ /~23 nm selenium film/p-CuSCN photovoltaic cell which generated a photocurrent of ~3.0  $\text{mA}/\text{cm}^2$ , a photovoltage of ~600 mV at 800  $\text{W}/\text{m}^2$  simulated sunlight and a maximum energy conversion efficiency of ~0.13%.

Vogel et al. in 1990 in *Chemical Physics Letters*, volume 174, page 241, reported the sensitization of highly porous  $\text{TiO}_2$  with in-situ prepared quantum size  $\text{CdS}$  particles (40-200Å), a photovoltage of 400 mV being achieved with visible light and high photon to current efficiencies of greater than 70% being achieved at 400 nm and an energy conversion efficiency of 6.0% under monochromatic illumination with  $\lambda = 460 \text{ nm}$ . In 1994 Hoyer et al. reported in *Applied Physics*, volume 66, page 349, that the inner surface of a porous titanium dioxide film could be homogeneously covered with isolated quantum dots and Vogel et al. reported in *Journal of Physical Chemistry*, volume 98, pages 3183-3188, the sensitization of various nanoporous wide-bandgap semiconductors, specifically  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{SnO}_2$  and  $\text{ZnO}$ , with quantum-sized  $\text{PbS}$ ,  $\text{CdS}$ ,  $\text{Ag}_2\text{S}$ ,  $\text{Sb}_2\text{S}_3$

and  $\text{Bi}_2\text{S}_3$  and the use of quantum dot-sensitized oxide semiconductors in liquid junction cells. The internal photocurrent quantum yield decreased with increasing particle diameter and decreased in the order  $\text{TiO}_2 > \text{ZnO} > \text{Nb}_2\text{O}_5 > \text{SnO}_2 > \text{Ta}_2\text{O}_5$ .

5 EP-A 1 176 646 discloses a solid state p-n heterojunction comprising an electron conductor and a hole conductor, characterized in that it further comprises a sensitizing semiconductor, said sensitizing being located at an interface between said electron conductor and said hole conductor; and its application in a solid  
10 state sensitized photovoltaic cell. In a preferred embodiment the sensitizing semiconductor is in the form of particles adsorbed at the surface of said electron conductor and in a further preferred embodiment the sensitizing semiconductor is in the form of quantum dots, which according to a particularly preferred embodiment are  
15 particles consisting of  $\text{PbS}$ ,  $\text{CdS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{Ag}_2\text{S}$ ,  $\text{InAs}$ ,  $\text{CdTe}$ ,  $\text{CdSe}$  or  $\text{HgTe}$  or solid solutions of  $\text{HgTe/CdTe}$  or  $\text{HgSe/CdSe}$ . In another preferred embodiment the electron conductor is a ceramic made of finely divided large band gap metal oxide, with nanocrystalline  $\text{TiO}_2$  being particularly preferred. EP-A 1 176 646  
20 further includes an example for making a layered heterojunction in which  $\text{SnO}_2$ -coated glass was coated with a compact  $\text{TiO}_2$  layer by spray pyrolysis,  $\text{PbS}$  quantum dots were deposited upon the  $\text{TiO}_2$  layer, the hole conductor 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)9,9'-spirobifluorene (OMeTAD) was deposited on the quantum dots and a  
25 semitransparent gold back contact was evaporated on the OMeTAD layer.

There is a need for nano-particles with improved stability for spectrally sensitizing nano-porous metal oxide semiconductor layers.

30 Aspects of the invention.

It is therefore an aspect of the present invention to provide improved spectral sensitization of nano-porous metal oxide semiconductors.

35 It is a further aspect of the present invention to provide a process for realizing improved spectral sensitization of nano-porous metal oxide semiconductors.

Further aspects and advantages of the invention will become apparent from the description hereinafter.

40 Summary of the invention.

It has been surprisingly found that spectral sensitization of nano-porous metal oxides on their internal and external surfaces with metal chalcogenide nano-particles is enhanced by the presence of a triazole or diazole compound.

5 Aspects of the present invention are realized by a nano-porous metal oxide semiconductor with a band-gap of greater than 2.9 eV in-situ spectrally sensitized on its internal and external surface with metal chalcogenide nano-particles with a band-gap of less than 2.9 eV containing at least one metal chalcogenide, wherein the nano-  
10 porous metal oxide semiconductor further contains a triazole or diazole compound.

Aspects of the present invention are also realized by a process for in-situ spectral sensitization of nano-porous metal oxide semiconductor with a band-gap of greater than 2.9 eV on its internal  
15 and external surface with metal chalcogenide nano-particles with a band-gap of less than 2.9 eV, containing at least one metal chalcogenide, comprising a metal chalcogenide-forming cycle comprising the steps of: contacting the nano-porous metal oxide with a solution of metal ions; and contacting the nano-porous metal oxide  
20 with a solution of chalcogenide ions, wherein the solution of metal ions and/or the solution of chalcogenide ions contains a triazole or diazole compound.

Aspects of the present invention are also realized by a photovoltaic device comprising the above-mentioned nano-porous metal  
25 oxide semiconductor.

Aspects of the present invention are also realized by a second photovoltaic device comprising a nano-porous metal oxide semiconductor with a band-gap of greater than 2.9 eV on spectrally sensitized on its internal and external surface with metal  
30 chalcogenide nano-particles with a band-gap of less than 2.9 eV, containing at least one metal chalcogenide, prepared according to the above-mentioned process.

Preferred embodiments are disclosed in the dependent claims.

35 Detailed description of the invention.

Figure 1 represents the dependence of absorbance [A] upon wavelength [ $\lambda$ ] in nm for: a, unsensitized nano-porous TiO<sub>2</sub> layer (. absorbance at 500 nm = 0.15); b, nano-porous TiO<sub>2</sub> layer sensitized with PbS  
40 with one dipping cycle (absorbance at 500 nm = 0.26); c, nano-porous TiO<sub>2</sub> layer sensitized with Bi<sub>2</sub>S<sub>3</sub> with one dipping cycle (absorbance at 500 nm = 0.28); d, nano-porous TiO<sub>2</sub> layer

sensitized with PbS with three dipping cycles (absorbance at 500 nm = 0.65); and e, nano-porous TiO<sub>2</sub> layer sensitized with Bi<sub>2</sub>S<sub>3</sub> with three dipping cycles (absorbance at 500 nm = 2.50).

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#### Definitions

The term nano-porous metal oxide semiconductor means a metal oxide semiconductor having pores with a size of 100 nm or less and having an internal surface area of at least 20 m<sup>2</sup>/g and not more  
10 than 300 m<sup>2</sup>/g.

The term chalcogenide means a binary compound containing a chalcogen and a more electropositive element or radical. A chalcogen is an element from group IV of the periodic table including oxygen, sulphur, selenium, tellurium and polonium.

15 The term "a mixture of two or more metal chalcogenides" includes a simple mixture thereof, mixed crystals thereof and doping of a metal chalcogenide by metal or chalcogenide replacement.

The term internal surface means the surface of pores inside a porous material.

20 The term in-situ spectrally sensitized means that the spectral sensitizer is formed where spectral sensitization is required.

The term aqueous for the purposes of the present invention means containing at least 60% by volume of water, preferably at least 80% by volume of water, and optionally containing water-miscible organic  
25 solvents such as alcohols e.g. methanol, ethanol, 2-propanol, butanol, iso-amyl alcohol, octanol, cetyl alcohol etc.; glycols e.g. ethylene glycol; glycerine; N-methyl pyrrolidone; methoxypropanol; and ketones e.g. 2-propanone and 2-butanone etc.

The term "support" means a "self-supporting material" so as to  
30 distinguish it from a "layer" which may be coated on a support, but which is itself not self-supporting. It also includes any treatment necessary for, or layer applied to aid, adhesion to the support.

The term continuous layer refers to a layer in a single plane covering the whole area of the support and not necessarily in direct  
35 contact with the support.

The term non-continuous layer refers to a layer in a single plane not covering the whole area of the support and not necessarily in direct contact with the support.

The term coating is used as a generic term including all means  
40 of applying a layer including all techniques for producing continuous layers, such as curtain coating, doctor-blade coating etc., and all techniques for producing non-continuous layers such as

screen printing, ink jet printing, flexographic printing, and techniques for producing continuous layers.

The abbreviation PEDOT represents poly(3,4-ethylenedioxythiophene).

5 The abbreviation PSS represents poly(styrene sulphonic acid) or poly(styrenesulphonate).

#### Nano-porous metal oxide semiconductor

10 Aspects of the present invention are realized by a nano-porous metal oxide semiconductor with a band-gap of greater than 2.9 eV in-situ spectrally sensitized on its internal and external surface with metal chalcogenide nano-particles with a band-gap of less than 2.9 eV containing at least one metal chalcogenide, wherein the nano-  
15 porous metal oxide further contains a triazole or diazole compound.

According to a first embodiment of the nano-porous metal oxide semiconductor, according to the present invention, the metal oxide semiconductor is n-type.

According to a second embodiment of the nano-porous metal oxide,  
20 according to the present invention, the metal oxide is selected from the group consisting of titanium oxides, tin oxides, niobium oxides, tantalum oxides, tungsten oxides and zinc oxides.

According to a third embodiment of the nano-porous metal oxide semiconductor, according to the present invention, the nano-porous  
25 metal oxide semiconductor is titanium dioxide.

#### Metal chalcogenide

Aspects of the present invention are realized by a nano-porous  
30 metal oxide semiconductor with a band-gap of greater than 2.9 eV in-situ spectrally sensitized on its internal and external surface with metal chalcogenide nano-particles with a band-gap of less than 2.9 eV containing at least one metal chalcogenide, wherein the nano-porous metal oxide further contains a triazole or diazole compound.

35 According to a fourth embodiment of the nano-porous metal oxide, according to the present invention, the metal chalcogenide is a metal oxide, metal sulphide, metal selenide or a mixture of two or more thereof.

According to a fifth embodiment of the nano-porous metal oxide,  
40 according to the present invention, the metal chalcogenide is a metal sulphide or a mixture of two or more thereof.

According to a sixth embodiment of the nano-porous metal oxide, according to the present invention, the metal chalcogenide is selected from the group consisting of lead sulphide, bismuth sulphide, cadmium sulphide, silver sulphide, antimony sulphide, indium sulphide, copper sulphide, cadmium selenide, copper selenide, indium selenide, cadmium telluride or a mixture of two or more thereof.

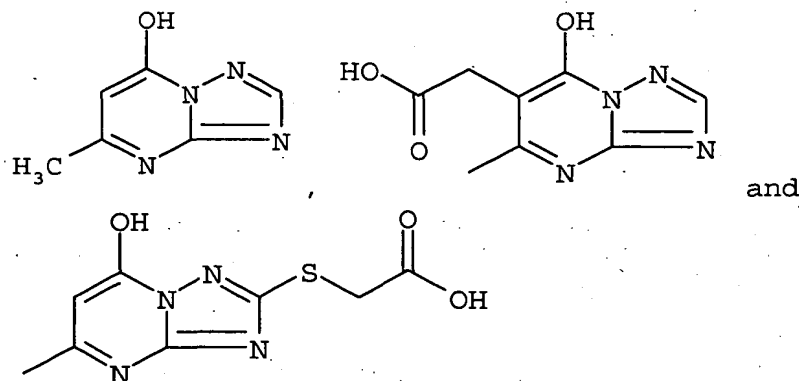
#### Triazole or diazole compound

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Aspects of the present invention are realized by a nano-porous metal oxide semiconductor with a band-gap of greater than 2.9 eV in-situ spectrally sensitized on its internal and external surface with metal chalcogenide nano-particles with a band-gap of less than 2.9 eV containing at least one metal chalcogenide.

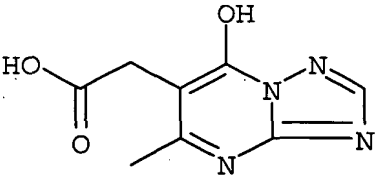
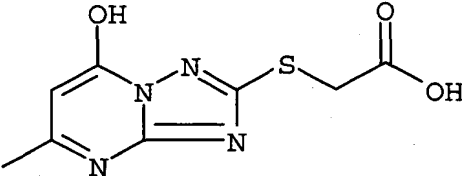
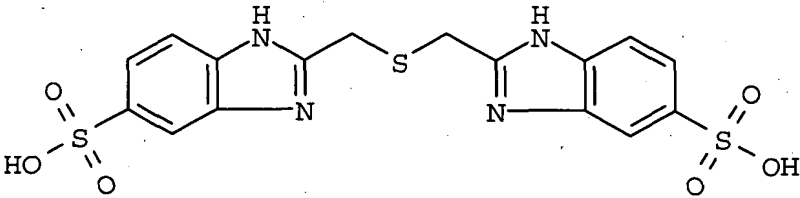
According to a seventh embodiment of the nano-porous metal oxide, according to the present invention, the triazole compound is a tetraazaindene.

According to an eighth embodiment of the nano-porous metal oxide, according to the present invention, the triazole compound is selected from the group consisting of



Suitable triazole or diazole compounds, according to the present invention, include:

T1		5-methyl-1,2,4-triazolo-(1,5-a)-pyrimidine-7-ol
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T2		
T3		
D1		

### Phosphoric acid or phosphate

According to a ninth embodiment of the nano-porous metal oxide,  
 5 according to the present invention, the nano-porous metal oxide further contains a phosphoric acid or a phosphate.

According to a tenth embodiment of the nano-porous metal oxide,  
 according to the present invention, the phosphoric acid is selected  
 from the group consisting of, orthophosphoric acid, phosphorous  
 10 acid, hypophosphorous acid and polyphosphoric acids.

Polyphosphoric acids include diphosphoric acid, pyrophosphoric acid, triphosphoric acid, tetraphosphoric acid, metaphosphoric acid and "polyphosphoric acid".

According to an eleventh embodiment of the nano-porous metal  
 15 oxide, according to the present invention, the phosphate is selected from the group consisting of orthophosphates, phosphates, phosphites, hypophosphites and polyphosphates.

Polyphosphates are linear polyphosphates, cyclic polyphosphates or mixtures thereof. Linear polyphosphates contain 2 to 15  
 20 phosphorus atoms and include pyrophosphates, dipolyphosphates, tripolyphosphates and tetrapolyphosphates. Cyclic polyphosphates contain 3 to 8 phosphorus atoms and include trimetaphosphates and tetrametaphosphates and metaphosphates.

Polyphosphoric acid may be prepared by heating  $\text{H}_3\text{PO}_4$  with  
 25 sufficient  $\text{P}_4\text{O}_{10}$  (phosphoric anhydride) or by heating  $\text{H}_3\text{PO}_4$  to remove water. A  $\text{P}_4\text{O}_{10}/\text{H}_2\text{O}$  mixture containing 72.74%  $\text{P}_4\text{O}_{10}$  corresponds to pure  $\text{H}_3\text{PO}_4$ , but the usual commercial grades of the acid contain more



water. As the  $P_4O_{10}$  content  $H_4P_2O_7$ , pyrophosphoric acid, forms along with  $P_3$  through  $P_8$  polyphosphoric acids. Triphosphoric acid appears at 71.7%  $P_2O_5$  ( $H_5P_3O_{10}$ ) and tetraphosphoric acid ( $H_6P_4O_{13}$ ) at about 75.5%  $P_2O_5$ . Such linear polyphosphoric acids have 2 to 15 phosphorus atoms, which each bear a strongly acidic OH group. In addition, the two terminal P atoms are each bonded to a weakly acidic OH group. Cyclic polyphosphoric acids or metaphosphoric acids,  $H_nP_nO_{3n}$ , which are formed from low-molecular polyphosphoric acids by ring closure, have a comparatively small number of ring atoms ( $n=3-8$ ). Each atom in the ring is bound to one strongly acidic OH group. High linear and cyclic polyphosphoric acids are present only at acid concentrations above 82%  $P_2O_5$ . Commercial phosphoric acid has a 82 to 85% by weight  $P_2O_5$  content. It consists of about 55% tripolyphosphoric acid, the remainder being  $H_3PO_4$  and other polyphosphoric acids.

A polyphosphoric acid suitable for use according to the present invention is a 84% (as  $P_2O_5$ ) polyphosphoric acid supplied by ACROS (Cat. No. 19695-0025).

process for in-situ spectral sensitization of nano-porous metal oxide with metal chalcogenide nano-particles

Aspects of the present invention are also realized by a process for in-situ spectral sensitization of nano-porous metal oxide semiconductor with a band-gap of greater than 2.9 eV on its internal and external surface with metal chalcogenide nano-particles with a band-gap of less than 2.9 eV, containing at least one metal chalcogenide, comprising a metal chalcogenide-forming cycle comprising the steps of: contacting nano-porous metal oxide with a solution of metal ions; and contacting nano-porous metal oxide with a solution of chalcogenide ions, wherein the solution of metal ions and/or the solution of chalcogenide ions contains a triazole or diazole compound.

According to a first embodiment of the process, according to the present invention, the contact with a solution of metal ions occurs before the contact with a solution of chalcogenide ions.

According to a second embodiment of the process, according to the present invention, the metal chalcogenide-forming cycle is repeated.

According to a third embodiment of the process, according to the present invention, the triazole or diazole compound is tetraazaindene is 5-methyl-1,2,4-triazolo-(1,5-a)-pyrimidine-7-ol.

According to a fourth embodiment of the process, according to the present invention, at the end of the metal chalcogenide-forming cycle the metal chalcogenide is rinsed with an aqueous solution containing a phosphoric acid or a phosphate.

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#### Support

Supports for use according to the present invention include polymeric films, silicon, ceramics, oxides, glass, polymeric film  
10 reinforced glass, glass/plastic laminates, metal/plastic laminates, paper and laminated paper, optionally treated, provided with a subbing layer or other adhesion promoting means to aid adhesion to adjacent layers. Suitable polymeric films are poly(ethylene terephthalate), poly(ethylene naphthalate), polystyrene,  
15 polyethersulphone, polycarbonate, polyacrylate, polyamide, polyimides, cellulose triacetate, polyolefins and poly(vinylchloride), optionally treated by corona discharge or glow discharge or provided with a subbing layer.

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#### Photovoltaic devices

Aspects of the present invention are realized by a photovoltaic device comprising the porous metal oxide semiconductor, according to the present invention.

25 Aspects of the present invention are realized by a second photovoltaic device comprising a porous metal oxide semiconductor produced according to the process, according to the present invention.

According to a first embodiment of the photovoltaic device,  
30 according to the present invention, the photovoltaic device comprises a layer configuration.

According to a first embodiment of the second photovoltaic device, according to the present invention, the photovoltaic device comprises a layer configuration.

35 Photovoltaic devices incorporating the spectrally sensitized nano-porous metal oxide, according to the present invention, can be of two types: the regenerative type which converts light into electrical power leaving no net chemical change behind in which current-carrying electrons are transported to the anode and the  
40 external circuit and the holes are transported to the cathode where they are oxidized by the electrons from the external circuit and the photosynthetic type in which there are two redox systems one

reacting with the holes at the surface of the semiconductor electrode and one reacting with the electrons entering the counter-electrode, for example, water is oxidized to oxygen at the semiconductor photoanode and reduced to hydrogen at the cathode. In the case of the regenerative type of photovoltaic cell, as exemplified by the Graetzel cell, the hole transporting medium may be a liquid electrolyte supporting a redox reaction, a gel electrolyte supporting a redox reaction, an organic hole transporting material, which may be a low molecular weight material such as 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)9,9'-spirobifluorene (OMeTAD) or triphenylamine compounds or a polymer such as PPV-derivatives, poly(N-vinylcarbazole) etc., or inorganic semiconductors such as CuI, CuSCN etc. The charge transporting process can be ionic as in the case of a liquid electrolyte or gel electrolyte or electronic as in the case of organic or inorganic hole transporting materials.

Such regenerative photovoltaic devices can have a variety of internal structures in conformity with the end use. Conceivable forms are roughly divided into two types: structures which receive light from both sides and those which receive light from one side. An example of the former is a structure made up of a transparently conductive layer e.g. an ITO-layer or a PEDOT/PSS-containing layer and a transparent counter electrode electrically conductive layer e.g. an ITO-layer or a PEDOT/PSS-containing layer having interposed therebetween a photosensitive layer and a charge transporting layer. Such devices preferably have their sides sealed with a polymer, an adhesive or other means to prevent deterioration or volatilization of the inside substances. The external circuit connected to the electrically-conductive substrate and the counter electrode via the respective leads is well-known.

Alternatively the spectrally sensitized nano-porous metal oxide, according to the present invention, can be incorporated in hybrid photovoltaic compositions such as described in 1991 by Graetzel et al. in Nature, volume 353, pages 737-740, in 1998 by U. Bach et al. [see Nature, volume 395, pages 583-585 (1998)] and in 2002 by W. U. Huynh et al. [see Science, volume 295, pages 2425-2427 (2002)]. In all these cases, at least one of the components (light absorber, electron transporter or hole transporter) is inorganic (e.g. nano-TiO<sub>2</sub> as electron transporter, CdSe as light absorber and electron transporter) and at least one of the components is organic (e.g. triphenylamine as hole transporter or poly(3-hexylthiophene) as hole transporter).

## Industrial application

Spectrally sensitized nano-porous metal oxide, according to the present invention, can be used in a both regenerative and photosynthetic photovoltaic devices.

The invention is illustrated hereinafter by way of reference and invention photovoltaic devices. The percentages and ratios given in these examples are by weight unless otherwise indicated.

## EXAMPLE 1

Preparation of solutions used in in-situ preparation of nano-sulphide particles

Metal solution 1:

Metal solution 1, a 0.6 M  $\text{Bi}^{3+}$ -solution, was prepared by mixing 36 mL of deionized water, 6.2 mL of concentrated  $\text{HNO}_3$  and 28.75 g of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , then adding a solution of 40 g triammonium citrate in 36 mL of deionized water and finally slowly adding 16 mL of a 50% NaOH-solution.

Metal solution 2:

Metal solution 2, a 0.96 M  $\text{Pb}^{2+}$ -solution, was prepared by dissolving 37.65 g of  $\text{Pb}(\text{NO}_3)_2$  in 100 mL of deionized water.

Sulphide solution 1:

Sulphide solution 1, a 0.1 M  $\text{S}^{2-}$  solution, was prepared by dissolving 0.78 g of  $\text{Na}_2\text{S}$  in 100 mL of deionized water.

Efficient adsorption of nano-sulphides on a nano-porous  $\text{TiO}_2$  layer.

A glass substrate (FLACHGLAS AG) was ultrasonically cleaned in ethanol for 5 minutes and then dried. A layer of a nano- $\text{TiO}_2$  dispersion (Ti-nanoxide HT Solaronix SA) was applied to the glass substrate using a doctor blade coater. This titanium dioxide-coated glass was heated to 450°C for 30 minutes. This results in a highly transparent nano-porous  $\text{TiO}_2$  layer. A dry layer thickness of 1.4  $\mu\text{m}$

was obtained as verified by laserprofilometry (DEKTRAK™ profilometer), mechanically with a diamond-tipped probe (Perthometer) and interferometry.

After the sintering step, the titanium dioxide-coated glass plates were cooled to 150°C by placing them on a hot plate at 150°C for 10 minutes and then immediately dipped into the metal solution for 1 minute, then rinsed for 10 seconds with deionized water immediately followed by dipping for 1 minute in the sulphide solution and finally rinsing once more with deionized water for 10 seconds. In this dipping cycle nano-metal sulphides were deposited on the internal and external surface of the nano-porous titanium dioxide. The amount of adsorbed nano-metal sulphide particles could be increased by carrying out multiple dipping cycles.

Absorption spectra between 200 and 800 nm were obtained using a Hewlett-Packard diode-array spectrophotometer HP 8452A. Figure 1 shows the absorption spectra for pure TiO<sub>2</sub>, TiO<sub>2</sub> with one cycle of Metal solution 1 (Bi<sup>3+</sup>) and Sulphide solution 1; and TiO<sub>2</sub> with one cycle of Metal solution 2 (Pb<sup>2+</sup>) and Sulphide solution 1. The absorption band is very broad and as a point of reference only the absorbance values at 500 nm will be given in the examples below.

Dipping cycles were carried out with Metal solutions 1 and 2 and Sulphide solution 1; and with the triazole compounds T1, T2 and T3 added to Metal solution 1, Metal solution 2 or to Sulphide solution 1 (7,5 ml of 10% solution of the triazole compound) in water was added to 50 ml of the metal or sulphide solution) as given in Table 1 and the absorbances at 500 nm of the resulting in-situ formed nano-metal sulphides determined, see Table 1.

Multiple dipping led to higher absorbances. The presence of a triazole in either the Metal solution or the Sulphide solution resulted in a more rapid increase in absorbance with the number of dippings. For Bi<sub>2</sub>S<sub>3</sub> it appears that this effect is stronger if the triazole is contained in the Sulphide-solution, whereas for the PbS, it appears that this effect is stronger if the triazole is contained in the Metal solution. Furthermore, the triazole T2 appears to be more favourable for in-situ Bi<sub>2</sub>S<sub>3</sub> nano-particle formation than T1 and T3 and the triazole T3 appears to be more favourable for in-situ PbS formation than T1 and T2.

Table 1:

Experi- ment nr.	Metal solution used	Metal sulphide formed	number of dipping cycles	triazole compound in metal solution	triazole compound in sulphide solution	Absorb- ance at 500 nm*
1 (comp)	1	Bi <sub>2</sub> S <sub>3</sub>	1	No	No	0.14
2 (comp)	1	Bi <sub>2</sub> S <sub>3</sub>	2	No	No	1.28
3 (comp)	1	Bi <sub>2</sub> S <sub>3</sub>	3	No	No	2.40
4 (comp)	1	Bi <sub>2</sub> S <sub>3</sub>	5	No	No	> 4
5 (inv)	1	Bi <sub>2</sub> S <sub>3</sub>	1	T1	No	0.12
6 (inv)	1	Bi <sub>2</sub> S <sub>3</sub>	1	No	T1	0.23
7 (inv)	1	Bi <sub>2</sub> S <sub>3</sub>	1	T2	No	0.18
8 (inv)	1	Bi <sub>2</sub> S <sub>3</sub>	1	No	T2	0.51
9 (inv)	1	Bi <sub>2</sub> S <sub>3</sub>	1	T3	No	0.10
10 (inv)	1	Bi <sub>2</sub> S <sub>3</sub>	1	No	T3	0.33
11 (inv)	1	Bi <sub>2</sub> S <sub>3</sub>	3	T1	No	> 4
12 (inv)	1	Bi <sub>2</sub> S <sub>3</sub>	3	No	T1	> 4
13 (comp)	2	PbS	1	No	No	0.12
14 (comp)	2	PbS	2	No	No	0.37
15 (comp)	2	PbS	3	No	No	0.59
16 (comp)	2	PbS	5	No	No	1.23
17 (comp)	2	PbS	7	No	No	2.47
18 (inv)	2	PbS	1	T1	No	0.24
19 (inv)	2	PbS	1	No	T1	0.10
20 (inv)	2	PbS	1	T2	No	0.18
21 (inv)	2	PbS	1	No	T2	0.17
22 (inv)	2	PbS	1	T3	No	0.32
23 (inv)	2	PbS	1	No	T3	0.19
24 (inv)	2	PbS	2	T1	No	0.61
25 (inv)	2	PbS	3	T1	No	1.30
26 (inv)	2	PbS	3	No	T1	0.63

\* corrected for the absorbance of TiO<sub>2</sub> at 500 nm (ca 0.15)

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## EXAMPLE 2

Evaluation in photovoltaic devices with liquid electrolyte

Photovoltaic devices 1 to 5 were prepared by the following  
10 procedure:

### *Preparation of the front electrode*

A glass plate ( $2 \times 7 \text{ cm}^2$ ) coated with conductive  $\text{SnO}_2:\text{F}$  (Pilkington TEC15/3) with a surface conductivity of ca 15 Ohm/square was ultrasonically cleaned in isopropanol for 5 minutes and then dried.

For these experiments Degussa P25  $\text{TiO}_2$  nano-colloid was used instead of the Solaronix colloid, 5 g of Degussa P25 being added to 15 mL of water with 1 mL of Triton X-100 being subsequently added. The resulting titanium dioxide colloidal dispersion was cooled in ice and ultrasonically treated for 5 minutes.

The electrode was taped off at the borders and was doctor blade-coated in the middle ( $0.7 \times 4.5 \text{ cm}^2$ ) with the above-described titanium dioxide colloidal dispersion to give layer thicknesses after sintering of  $2.0 \text{ }\mu\text{m}$  to ensure comparable optical absorbances of the cells. The sintering procedure and dipping procedure were as described for EXAMPLE 1. The front electrode was thereby produced, which was immediately used in assembling the cell.

### *Cell assembly*

The back electrode (consisting of  $\text{SnO}_2:\text{F}$  glass (Pilkington TEC15/3) evaporated with platinum to catalyse the reduction of the electrolyte) was sealed together with the front electrode with inbetween two pre-patterned layers of Surlyn<sup>®</sup> (DuPont) ( $2 \times 7 \text{ cm}^2$  where in the middle  $1 \times 6 \text{ cm}^2$  had been removed). This was performed at a temperature just above  $100^\circ\text{C}$  on a hotplate. As soon as the sealing was completed, the cell was cooled to  $25^\circ\text{C}$  and electrolyte was added through holes in the counter electrode. The electrolyte used was a solution of 0.5 M LiI, 0.05 M  $\text{I}_2$  and 0.4 M t-butylpyridine in acetonitrile and was injected into the cell during cell assembly. The holes were then sealed with Surlyn<sup>®</sup> and a thin piece of glass. Conductive tape was attached on both long sides of the cell to collect the electricity during measurement.

Measurements were performed immediately after the cell assembly.

### *Device characterisation*

The thereby prepared photovoltaic cells were irradiated with a Xenon Arc Discharge lamp with a power of  $100 \text{ mW/cm}^2$ . The current generated was recorded with a Keithley electrometer (Type 2420). The open circuit voltage ( $V_{\text{oc}}$ ), short circuit current density ( $I_{\text{sc}}$ ) and Fill

Factor (FF) of the photocell as calculated from the quality of generated current are given in Table 3.

Table 3:

Device nr	Metal sulphide	number of dipping cycles	triazole compound in Metal solution	triazole compound in Sulphide solution	I <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	FF
1 (comp)	PbS	1	No	No	0.35	0.540	0.37
2 (comp)	PbS	2	No	No	0.44	0.463	0.42
3 (comp)	PbS	3	No	No	0.64	0.460	0.31
4 (inv)	PbS	1	T1	No	0.68	0.580	0.55
5 (inv)	PbS	2	T1	No	0.46	0.560	0.42

The absorbance values for the adsorbed in-situ formed lead sulphide nano-particles were not determined. However, the values reported above for Experiments 5, 10, 11, 14 and 16 (see Table 1) for lead-sulphide nano-particles adsorbed on Solaronix titanium dioxide under the same conditions can be used as a guide.

From Table 3 it can be concluded that cells made with one dipping cycle with the triazole compound T1 show much better photoresponses than cells with one, two or even three dipping cycles in the absence of the triazole compound T1.

The present invention may include any feature or combination of features disclosed herein either implicitly or explicitly or any generalisation thereof irrespective of whether it relates to the presently claimed invention. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

Having described in detail preferred embodiments of the current invention, it will now be apparent to those skilled in the art that numerous modifications can be made therein without departing from the scope of the invention as defined in the following claims.

All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

The use of the terms "a" and "an" and "the" and similar referents in the context of describing the invention (especially in



the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Of course, variations of those preferred embodiments will become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practised otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.